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# The Metallurgist.

*Supplement to* **The Engineer**, *February, 1928.*

## Metallurgical Materials.

THOSE who are concerned with materials as engineers or users of engineering products naturally think of the materials to be tested as metals in various forms. They are apt to forget that there is a whole class of substances which are the materials of the metallurgist, whether he works at the reduction of metals from their ores, at their subsequent refining, or at their working up into the cast or wrought materials of engineering. Among these we may readily name such substances as fuel—coal or coke—and the refractory bodies of which furnaces of all kinds have to be constructed. If we go a little further we come to the moulding sands used by every foundry, whether ferrous or non-ferrous, and a great number of accessory materials. We have learnt to appreciate the fact that if we desire to maintain uniform success in our engineering products we must employ the best and most thorough means of testing the materials put into them. It is doubtful, however, whether metallurgists generally have yet come to a full appreciation of the corresponding facts in regard to materials of the kind we have indicated above. For some few of them there are specifications in use, but in many instances these rely almost exclusively on chemical analysis, and there would seem to be room and need for considerable further progress in that direction.

The suggestion that standard tests and specifications should be devised for all such materials is sometimes met by the argument that the properties required are so peculiar and complex, the products themselves so variable from uncontrollable causes, that any attempt at closely defined testing must fail. A further argument is that the uses of these materials are of a "rough-and-ready" nature and that anything like delicate and accurate testing methods and appliances are lacking in the places where these things are used, and would be out of place and could not be used there. A little reflection, however, will show that similar arguments are used, even in regard to metals, whenever any attempt is made to introduce a refinement into existing testing methods. It seems to be an inherent characteristic of human nature—and especially of human nature as we meet it in British foundries and metal works—to dislike and to suspect all innovations. The practical man is apt to think that by applying a more accurate or delicate test to any material the difficulty of production will be immediately increased. Experience has shown the exact opposite. The more we know of the nature and properties of the materials we produce, as well as of those we use, the better are we able to produce them with regularity and certainty of the required quality. There is nothing that will help us to know and understand our materials better than the systematic application of the most searching tests we can devise—provided that these tests themselves are based on sound principles and yield results which have a direct relation to the real value of the material. In regard to metals there is at the present time at least a beginning of a recognition of these facts, and manufacturers and users have to a large extent learnt that they can co-operate with great advantage to both in devising and agreeing upon testing methods, and that it is by no means to the advantage of the producer that tests should be kept unduly easy. The more progressive type of metal manufacturer, whether ferrous or non-ferrous, realises that he can meet stringent requirements better than his less competent rival. But in regard to fuels, refractories and sands the position is still much less fully developed.

As regards fuel, perhaps the outstanding question is that of the essential qualities of "metallurgical" coke. It is not yet settled whether crushing strength, resistance to abrasion or chemical reactivity is the most important property and how at all events the first two are best to be determined. There are, however, indications that these problems are being attacked; at least two Committees are at work at the present time on the investigation of coke. On refractories a good deal of work has been done in regard to testing, but most of it has come from abroad, and we have reason to believe that the systematic testing of refractories has been developed much further there—and especially in Germany—than here. Yet the value of refractories consumed annually by our metallurgical, gas, glass and ceramic industries must be very great. A small percentage on the annual expenditure involved would do much to clear up these questions of how best to test refractories for various purposes. For instance, what is known rather inelegantly as the "squatting test" for refractories was first developed to any large extent in Germany; it is still associated with the name of a German investigator—Seger—whose well-known "cones" are widely used; fortunately, these are now obtainable of British manufacture, but even that is only a war-time or post-war development. This "squatting test," it may be recalled, consists in determining, by comparison with a series of cones of known composition and properties, the temperature and duration of heating under which a small sample cone of the refractory under test will "squat"—*i.e.*, become so soft as to collapse under its own weight. This type of test has, of course, been adopted instead of a determination of the "melting point" because these complex refractory substances do not melt in a homogeneous manner, but undergo gradual softening into a viscous condition.

Unfortunately, this "squatting test" is not a satisfactory means of establishing the heat-resisting powers of a refractory. Such a material becomes useless in a furnace long before it has grown soft enough to collapse under its own weight, and it is

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found that the relative merit of different materials in practical use does not correspond well with their squatting temperatures. Evidently something more is required and a test for "refractoriness under load" has been developed by several workers. Here the temperature of collapse is again determined, but under an applied load. This appears to offer information of much greater value, but it is a test which does not seem to have found any wide application in this country, although special appliances for making it are commercially available on the Continent. There is, we believe, a British Refractories Research Association, but very little has been heard of its activities. and nothing in the nature of standard tests for refractories appears to have been developed, or, if they have, knowledge of them has not gone far beyond the inner circle of those directly concerned.

Matters of this kind, it may be suggested, are domestic to the builder of furnaces, but even that is in itself an important branch of engineering, so that general interest attaches to its problems. This is particularly important at a time when British metallurgical industries are engaged in a severe industrial struggle. Economy in the working of furnaces is dependent on the good behaviour of furnace walls and linings, from the blast-furnace down to the pots in which aluminium or even solder is melted. In the past the industries of this country have been favoured with an easy supply of natural materials, available on the spot and meeting all the requirements of the local industry. As industry has developed the requirements have become more severe and in many cases the qualities of local natural products have deteriorated owing to gradual exhaustion or impoverishment of the deposits. Yet we are inclined to cling to brands of products based on these natural supplies and to accept them as the best possible without much test or inquiry. That method, however, cannot in the long run meet present-day requirements, and the necessity of applying modern methods of testing to these materials—although it entails many difficulties—is becoming increasingly evident.

## Iron Castings or Steel?

CAST iron, so long the Cinderella of metallurgy, appears at last to be coming to some extent into its own. We have published from time to time in THE METALLURGIST articles and review-abstracts dealing with recent work on the subject, both in this country and in America and Germany, and in the present issue we commence the publication of an instructive review of modern developments by Mr. J. G. Pearce, the director of the British Cast Iron Research Association. Anyone who has followed these developments cannot fail to realise that while a good deal has been done to apply modern methods to the special problems of cast iron, a very great deal still needs to be done before we can regard that branch of metallurgy as being brought to a level with that of steel or the non-ferrous metals. This applies both to the scientific and the practical side. While the Cast Iron Research Association is struggling, under very difficult conditions, to do its best for the progress of the subject, it is so hampered by insufficient funds and support, that it can undertake very little of the more far-reaching types of research. It is doing excellent work and deserves the fullest support of the industry and of the Government, but it is still not able to do one-quarter of what ought to be done for so important an industry. And in this connection, it is worth while to notice that there is an important industrial field which lies, even at the present time, on the borderland between cast iron of the best type and cast steel. Mr. Pearce draws attention to the way in which, for certain purposes, practice has swung around from cast iron to steel and back again. It is, of course, not at all likely that steel castings will ever invade the field covered by the cheapest kinds of iron castings, where price is almost the only important factor, but there are many uses where the higher cost of steel may be counterbalanced by better physical properties, which allow of a reduction of size and weight. It is, therefore, imporant for the ironfounder, interested in the higher grade of castings used for engineering construction, to see that the rapid advances of steel metallurgy do not leave him behind. Co-operative effort, such as that represented by the research associations, is probably his only safeguard, but it is essential that it should be supported on a far larger scale than it is at present.

It is interesting to notice, in discussions on recent developments of cast iron, that there is a certain limit which those interested in cast iron always desire to avoid—it is the limit where the "difficulties associated with the production of steel castings" are approached. The exact type of difficulty considered appears to vary in different instances. Sometimes, it appears to be regarded as essential that cupola melting should be retained, and this involves a number of limitations. The temperature that can be reached is limited, the carbon content can only be kept down with difficulty, and the contamination of the metal with impurities derived from the coke cannot be avoided. It is, of course, perfectly true that the cupola is a very economical melting appliance, and that the use of other types of furnace is comparatively expensive, as matters stand at present. It may, however, remain to be seen in the future whether more modern methods of melting may not discount this difference to a considerable extent when the value of the product is taken into account.

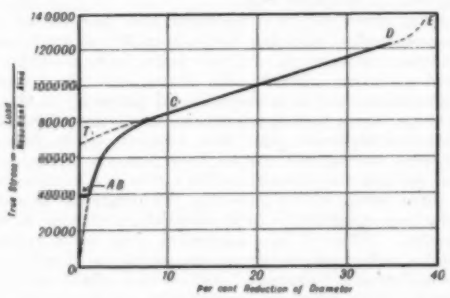
Even more serious, perhaps, are the casting difficulties which are associated with the use of steel as compared with cast iron. Not only is the latter more fluid and cast at a lower temperature, but the tendency to produce unsound castings, either as the result of shrinkage or of gas evolution, is much smaller. The lower temperature, of course, avoids the well-known difficulties connected with steel moulding sands, while the much smaller risk of unsound castings is an important factor in cost. But it must be borne in mind that these are metallurgical advantages which cast iron gains at the expense of quality. High-carbon and high-phosphorus are essential to fluidity at low temperatures, but these factors militate against strength and ductility. On the other hand, the present difficulties of steel casting may well be overcome by metallurgical advances. Much active research is in progress in this field, and it may well happen that means will be found of largely freeing steel from its gas content, of reducing its solidification contraction and of providing satisfactory mould material without increasing the cost of the product appreciably—in fact, if the regularity of the product is improved that alone will tend to cheapen it. All this, of course, is to the good. A struggle between steel castings and iron for the field that might be covered by either will make for the advancement of both steel and cast iron. It is, in fact, from such

industrial battles that the most rapid technical progress often results. We have seen this in the past in the contest between armour plate and armour-piercing shell; we see it at the present time in the struggle between the high-pressure steam plant and the internal combustion engine; and it is quite likely that we may see it in the near future—if we have not already entered upon it—between high-class iron castings and those made of steel. It is, however, very important that the ironfounder, and particularly the British ironfounder, should not let the struggle go by default. It is essential that he should take a long view and use to the full the means and organisations already to his hand.

## The Strength of Cold-worked Steel.*

The increasing tendency to use cold-worked steel has drawn attention to the need for more information regarding the relation between stress and deformation beyond the elastic limit. The data derived from an ordinary tensile test, viz., yield point, ultimate stress, elongation and reduction of area are inadequate for the selection of a material when its condition is modified by previous stressing above the elastic limit.

On consideration, it would seem that the stress-strain curve, as usually drawn, does not accurately represent a relation between two interdependent variables above the ultimate tensile strength, since, on account of the necking that takes place in this region, the total elongation has no direct relationship to the stress carried by the specimen. It is the area at the neck that controls this stress, and it seems therefore more logical to correlate the stress with the reduced diameter at the constriction. This fact was realised by Stead, who plotted the results of tensile tests as true stress—that is, total applied load divided by minimum area at the neck—against percentage reduction of diameter, and obtained in this manner a curve such as that shown below. In this




diagram, A B corresponds to the flow immediately after the yield point is reached. C corresponds to the maximum load or ultimate tensile strength, as found in the ordinary tensile test. The portion of the curve between C and D represents that part of the test in which local elongation and reduction of area occur, and is found to be linear nearly up to rupture, which is represented by E.

Since the true stress increases with cold working, and the amount of cold working may be represented by the reduction of area, it is not altogether surprising that a rather striking similarity is found between stress-strain curves of this type for different steels. The author has analysed Stead's results, supplemented with some of his own, and has found a feature to which Stead did not refer, namely, that if the straight line D C is produced to cut the stress axis, it does so at a point T which represents the ultimate tensile strength based on the original area. The author's curves were obtained from ten tests of six different chrome and chrome-nickel steels with different heat treatment, and he found that these, together with Stead's curves, could be represented very closely by the general empirical expression—

$$S = T + 0{\cdot}2\sqrt{T}x - T^{(1-0{\cdot}0018Tx)}$$

where T is the ultimate tensile strength, based on original area, in thousands of pounds per square inch, $x$ is the percentage reduction in diameter, and S is the true stress in thousands of pounds per square inch.

The value of S obtained in this way will represent the resistance per unit of minimum area which the steel will exert at the end of cold working to a given reduction of diameter. Since, also, a specimen that has been stressed to a given value and then relieved of load becomes elastic up to this stress when the load is re-applied, the value of S obtained by the use of the above expression should indicate the approximate yield point of cold-worked steel.

* See *Engineering News-Record*, Vol. 99, No. 14, page 548, Earle B. Norris.

## Ferrous Oxide.

A considerable number of researches have been published on the preparation of ferrous oxide, amongst others, by Debray[1], Hilpert and Beyer,[2] Chaudron,[3] Wohler and Gunther,[4] Lepetit,[5] Matsubara,[6] and Schenck.[7] These workers for the most part rely on the old explanation of the distribution of the solid phase in the Baur-Glässner diagram, whereas Schenck, in his later work on the equilibrium of the system Fe-O-C, places the stability of ferrous oxide in the upper equilibrium line. Chaudron and also Wyckoff and Crittenden[8] burned iron in oxygen, and remelted the oxide thus produced with iron. The product was described as consisting essentially of ferrous oxide.

In a recent research Groebler and Oberhoffer[9] used the reduction of iron oxide in a mixture of carbon monoxide and dioxide as offering the best prospect for the preparation of pure ferrous oxide. They heated iron oxide contained in an alundum boat in a stream of carbon monoxide and dioxide in various proportions, the temperature and other conditions being carefully controlled. Equilibrium with any particular gas mixture was ascertained when the weight of reaction product remained constant.

A large number of preliminary experiments were

[1] *Comptes rendus*, 45, 1857.
[2] *Ber. D. Chem. Ges.*, 44, 1911.
[3] *Comptes rendus*, 159, 1914, 172, 1921; *Rev. Met.*, 21, 1924.
[4] *Z. Elecktrochem.*, 29, 1923.
[5] "Dissertation," Münster, 1922.
[6] "Trans.," Am. Inst., Min. Met. Eng., 67, 1922.
[7] *St. u. E.*, 46, 1926.
[8] *J.*, Am. Chem. Soc., 47, 1925.
[9] *St. u. E.*, Nov. 24th, 1927.

made at a temperature of 800 deg. Cent. The reaction products were analysed and the results checked by the loss in weight of the sample. The results indicated that, in the ferrous oxide field of the Baur-Glässner diagram, a mixture of ferro-ferric and ferrous oxides is present, the content of ferro-ferric oxide decreasing with increasing carbon monoxide. Above the upper equilibrium line a large quantity of iron separates. With 66 per cent. of carbon monoxide the line was fixed at 800 deg. Cent. The purest product contained 99·3 per cent. (?) ferrous oxide and 0·7 per cent. ferro-ferric oxide. Using larger quantities of about 6 grammes of ferric oxide, the longer time required for reduction—eight to ten hours—made temperature control more difficult, and a less pure product was obtained with 95 per cent. ferrous oxide, some ferro-ferric oxide and metallic iron.

The degree of purity of the ferrous oxide depended on the regulation of the gas mixture and the maintenance of constant temperature. In order to avoid these difficulties, a second method was tried. Between 800 deg. and 830 deg. Cent., with a gas mixture containing 72 to 76 per cent. carbon monoxide and a reduction period of eight hours, a product was obtained with 15 to 25 per cent. of metallic iron and free from ferro-ferric oxide. When the metallic iron was dissolved out, the residue contained 95 per cent. of ferrous oxide.

Groebler and Oberhoffer examined various methods for dissolving out the metallic iron and for the analysis of the constituents of the solid phase. This can consist of ferric oxide, ferro-ferric oxide, ferrous oxide and iron. The stability of ferric oxide lies practically at 100 per cent. carbon dioxide, so that when carbon monoxide is present all the trivalent iron may be regarded as $Fe_3O_4$.

After a study of other methods, the authors adopted the mercuric chloride method for the estimation of metallic iron, although it was not suitable for the subsequent examination or use of the residue.

The method was introduced by Wilner-Merck[10] and afterwards investigated by Ingeberg[11] and Frerichs and Coblentz[12], who found that time and temperature combined with small mass influenced the results. The effect of high temperature—boiling point—shortens the time for the solution of the iron and with large mass counterbalances the action of the solution on ferrous oxide.

The divalent iron was determined by the method of Zimmerman and Reinhardt. A reduction of trivalent iron by the hydrogen evolved during solution in hydrochloric acid by the metallic iron present was not noted. The amount of trivalent iron was calculated from the difference between divalent and total iron and also determined by the iodine method, using a finely graduated burette. The values obtained by the two methods were in good agreement.

The authors state that by melting in vacuo the composition of ferrous oxide is only changed by 0·1 per cent. The melting point was therefore determined in the following way:—The powdered oxide was pressed into rods, 4 mm. diameter and 10 mm. long, under a pressure of 1500 kilos. to 2000 kilos., a short platinum wire being forced into one end. The rods were suspended vertically in a Pythagoras tube heated in a Silit furnace. The tube was fitted with a cooled cap and evacuated. The sample was sighted from above by a pyrometer through the glass dome of the cooling cap. The temperature was noted when the rod dropped off. Readings were taken by a number of observers in order to reduce personal errors. The method has the advantage that the ferrous oxide does not come into contact with any refractory material or with the thermo-couple, and the observation of liquefaction is instantaneous. The observed melting point is subject to correction for the absorption coefficient of the glass dome, and the emissivity of the sample according to Fry.[13] The samples used contained from 76·1 to 95·5 per cent. of ferrous oxide, and by extrapolation the melting point of pure ferrous oxide was found to be 1377 deg. Cent. Rosenhain, Hanson and Tritton[14] by a different method obtained a value of 1371 deg. Cent.

### X-RAY EXAMINATION.

The problem of the formation of solid solutions between $Fe_3O_4$ and FeO has given rise to lively discussion. Matsubara by the introduction of the decomposition diagrams of iron oxide at constant temperatures found the means of solving this problem. But as the points for pure ferrous oxide in these diagrams are not clear, Groebler and Oberhoffer prepared a series of X-ray photographs of samples of oxide reduced at 800 deg. Cent., so that a direct comparison could be made with the decomposition diagram. The Debye-Scherrer method was used, the sample being fastened on a yarn thread with collodion. The samples with up to 5 per cent. ferrous oxide showed a displacement of the interference bands owing to the presence of a solid solution. With 58 per cent. ferro-ferric oxide and 42 per cent. ferrous oxide, which is on the middle horizontal of the decomposition curve, new lines appeared which proved to be the ferrous oxide lines. These were the only lines present in the oxides, situated on the middle S form part of the decomposition curve, containing up to 88·8 per cent. of ferrous oxide. These lines were also found unchanged beside the lines of metallic iron in the samples situated on the upper horizontal, which contained 97·8 to 85·4 per cent. ferrous oxide and 1·5 to 14·6 per cent. of metallic iron.

From these results it appeared that at a reduction temperature of 800 deg. Cent. ferro-ferric oxide can contain a maximum of 5 per cent. ferrous oxide in solid solution. Above this percentage the ferrous oxide exists free as a second solid phase up to about 31·9 per cent. ferro-ferric-oxide, when the magnetite lattice disappears and the ferrous oxide lattice remains unchanged up to pure ferrous oxide. In this section the decomposition curve is a continuous S form bend, which indicates the existence of solid solutions apparently in contradiction of the X-ray results. Hüttig[15] has suggested that in a crystal lattice under certain circumstances a constituent can occur free as a "vagrant," and his example of uranium dioxide and oxide is remarkably similar to ferro-ferric and ferrous oxide. According to this assumption, ferrous oxide can contain up to about 31·9 per cent. ferro-ferric oxide in its lattice without change in the structure or magnitude, the excess oxygen being free vagrant in the lattice. There are, however, serious difficulties in the way of accepting Hüttig's assumption. The solubility of iron in ferrous oxide can, if it exists at all, be only very slight, as there is no displacement of the ferrous oxide lines in the pre-

[10] *Z. Anal. Chem.*, 41, 1902.
[11] *Ind. Eng. Chem.*, 17, 1925.
[12] *Z. Angew. Chem*, 22, 1909; *Arch. d. Pharm.*, 146, 1908.
[13] *Krupp. Monatsh.*, 4, 1924.
[14] *J.*, Iron Steel Inst., 60, 1924.
[15] *Physik und Phys. Chem.*, 18, 1924.

parations consisting of ferrous oxide with some metallic iron. In contrast to this, there is a displacement of the iron lines, indicating solid solution of ferrous oxide in iron. Rosenhain, Hanson and Tritton estimated that the solid solubility of oxygen in iron is about 0·05 per cent. oxygen.

The point corresponding to pure ferrous oxide lies in the transition of the middle S form part to the upper horizontal of the decomposition curve, not as Matsubara and also Eastman[16] assumed in the turning point of the S part of the curve. Contrary to the view of these workers, no solid solution of iron in ferrous oxide exists. The supposition of Wyckoff and Crittenden that no solid solution exists between ferro-ferric oxide and ferrous oxide depends on the fact that their preparations lie on the middle horizontal of the decomposition curve.

The criticism of Groebler and Oberhoffer of the assumption of Matsubara regarding the position of the point for pure ferrous oxide is difficult to understand, as the published results appear to the writer to be in agreement. The real difference that exists is that Matsubara indicates the possibility of a solid solution of $Fe_3O_4$ in FeO and also of metallic iron in FeO. Wyckoff and Crittenden only made use of three preparations which were obtained by a fusion method and these appear to be situated, not on the middle horizontal as stated above, but between the transition from the middle horizontal and the steep slope joining this to the upper horizontal. The chief difference between their preparations and those of Groebler and Oberhoffer is that in the former, owing to the method of preparation, metallic iron occurs associated with both $Fe_3O_4$ and FeO in the same mixture, whereas in the latter metallic iron is practically only present in association with FeO. Wyckoff and Crittenden found in one of their preparations with about 43 per cent. ferro-ferric oxide and 52 per cent. ferrous oxide some slight evidence of solid solution of ferro-ferric oxide in ferrous oxide and, as Groebler and Oberhoffer do not appear to have explored this region, further X-ray examination of such preparations is necessary.

Although Groebler and Oberhoffer obtained equilibrium between the solid and the gaseous phase, it does not follow that equilibrium was obtained between the constituent phases of the solid portion, and this may account for the apparent contradiction between the X-ray and decomposition curve results and may have some bearing on the conclusion that ferrous oxide can take up a considerable amount of ferro-ferric oxide without change in the lattice.

[16] *J.*, Am. Chm. Soc., 44, 1922.

## Aluminium Bronze.

*(From a Correspondent.)*

No. I.

Aluminium bronze appears to date back about seventy years, when the late Dr. Percy first prepared "aluminium gold," as it was then called. At that time, however, there was difficulty in applying the alloy to practical purposes on account of the high price of aluminium. The present day product is, by virtue of the greater purity of modern aluminium, a much superior material, and there is a growing demand for this alloy for engineering uses, on account of its valuable properties, and its applications are likely to extend. The term "aluminium bronze" is really a misnomer, since it has been agreed by the Nomenclature Committee of the British Institute of Metals that the term "bronze" is correctly applied only to copper alloys containing tin, but the term has come into such general use that its discontinuance would be confusing.

### Colour.

The usual 10 to 11 per cent. aluminium-copper alloy of commerce has a rich golden colour. With the addition of aluminium to copper, the latter quickly loses its characteristic colour, becoming paler. Four to 8 per cent. of aluminium changes the colour from a deep to a pale gold. With a further addition of aluminium there is a gradual darkening of the pale gold through various reddish tints to about 18 per cent., after which the colour changes to that of steel, becoming with 25 per cent. aluminium silvery white. From 26 to 100 per cent. of aluminium there is no change in the colour.

### Corrosion Resistance.

These aluminium-coppers have been tested by prolonged exposure to the sea for periods of several years by complete immersion, and also for a similar time between wind and water. The alloy containing 10 per cent. of aluminium is extremely resistant to corrosion under these conditions, the test pieces having lost weight only to a minute extent. These alloys can also be exposed to a red heat in an oxidising atmosphere for several days without becoming appreciably tarnished by oxidation. The explanation is probably that a thin skin of aluminium oxide forms on the outer surface and prevents further oxidation. Although this is a great advantage, there is a compensating disadvantage in that the pellicle of oxide renders soldering extremely difficult in comparison with brass or tin-bronze.

The applications of so valuable a material are obviously very numerous. A recent popular use of the alloy has been the manufacture of articles of jewellery, such as cigarette cases, which, when nicely finished, bear a strong resemblance to polished gold, and have been sold under such fanciful titles as "orium" and "algold."

With regard to engineering applications, a notable case illustrating the utility of this material is the worm wheel used in the Ford motor truck, of which 1000 are required every day. Among a great variety of uses on board sea-going ships may be mentioned propellers, pumps, bearings and bushes. In the chemical industries the alloy is of great value, being used for tie rods, bolts, diaphragms, &c., of pickling equipment. Aluminium bronzes are, in fact, in great demand where exceptional strength and resistance to both corrosion and wear are essential.

### Machinability.

Aluminium bronze is a little more difficult to machine than other bronzes and brasses, although this does not mean that there is any great difficulty associated with this process. It is necessary to have very sharp tools, use higher speeds and provide ample lubrication. When these precautions are taken there is no more difficulty than with the other alloys mentioned. Aluminium bronze closely resembles mild steel in its machinability.

### Compositions, Melting and Fluxes.

It is essential that the component metals used

should be free from arsenic, antimony and phosphorus, which are undoubtedly harmful. For this reason electrolytic copper should be employed, although ordinary commercial grades of aluminium ingot are satisfactory. The iron content would not be objectionable, so long as it is known. Silicon should be practically absent, since about 0·1 per cent. considerably reduces the elongation of the resulting alloy.

A further reason for the avoidance of copper other than electrolytic is that fire smelted brands contain oxide in the form of $Cu_2O$, which, when aluminium is added, gives rise to intense heat, owing to the formation of aluminium oxide. The aluminium oxide is extremely objectionable in the alloy, since it forms little hard drossy patches, which considerably add to the founders' difficulties when the castings have to be machined and these patches are discovered.

The best proportion of aluminium to employ depends upon the properties which are required, since all the alloys containing up to 11 per cent. aluminium are serviceable, and the mechanical properties continually improve until 11 per cent. is reached. The addition of iron, which will be referred to later, enables a higher content of aluminium to be employed, without brittleness ensuing and with the attainment of still higher mechanical properties.

The melting point of the 10 per cent. alloy is about 1030 deg. Cent. (1886 deg. Fah.), while the melting point of copper is 1084 deg. Cent. (1980 deg. Fah.). It is a good plan, therefore, first to melt the copper under a cover of charcoal dust, and then to add the aluminium in the solid state, stirring carefully with a graphite stick afterwards. No excessive heat is generated provided electrolytic copper is used and is protected from oxidation during melting. The white heat which is often recorded as occurring on the addition of aluminium, which is so destructive to crucibles, is due to the combination of aluminium with copper oxide in the copper, resulting in aluminium oxide being formed and set free. Nothing is gained by using a 50 per cent. aluminium-copper alloy for the addition to the molten copper. When the charge is molten, the charcoal can be removed from the surface by blowing upon it with a pair of bellows.

There is no advantage in using any flux, since fluxes tend to destroy the crucibles; moreover, there is the possibility that small shots may remain in the alloy, causing localised corrosion at a later date. It has been claimed that there is an advantage in remelting the alloys before pouring them into the moulds, but experiment has shown that there is no advantage in doing this, at any rate, in the case of small castings. When large castings are to be made it is a good plan to pour the metal into dry sand moulds to form large blocks, say, the size of a brick, and then to remelt these before pouring into the actual moulds. The object of this procedure is to eliminate dissolved gases which are expelled from the metal as it solidifies slowly in the sand mould of low thermal conductivity.

### INFLUENCE OF IRON.

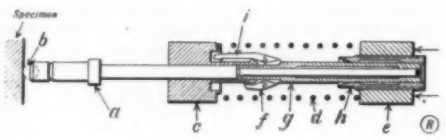
It has already been indicated that the addition of iron is distinctly beneficial to aluminium bronzes. Considerable prejudice exists among brass founders to the use of iron in their alloys, and this prejudice is well founded since in copper-zinc alloys iron is insoluble, forming small steely pellets, which are found distributed throughout the casting and blunt the machinist's tools when he cuts into them. When zinc is replaced by aluminium, however, the case is quite different, iron being soluble in the aluminium-copper alloy to a considerable extent. It is immaterial whether wrought or cast iron be used for making the additions, but it is generally best to employ wrought iron or mild steel, such as thin sheet clippings.

When cast iron is used, the carbon is ejected by the aluminium and floats to the surface as graphite flakes and dust. There is no chance of segregation with the small amount of iron usually alloyed in aluminium bronze.*

The alloys containing iron show properties markedly superior to those without iron, although at one time iron was considered distinctly objectionable in the manufacture of aluminium bronze. The result is that there is now a large selection of alloys from which to choose according to the purpose to which the material is to be applied. Usually not more than 4 per cent. of iron is added, but for a large range of work not more than 1 per cent. is used. A composition suitable for most ordinary purposes is copper, 88 per cent.; aluminium, 10 per cent.; iron, 1 per cent.; 30 per cent. manganese-copper, 1 per cent. The strength of this alloy should be much more than 80,000 lb. per square inch, and the elongation 20 to 30 per cent. A bronze giving 90,000 lb. per square inch with 20 to 35 per cent. elongation contains copper, 84 per cent.; aluminium, 10 per cent.; iron, 4 per cent.; 30 per cent. manganese-copper, 2 per cent. For very large castings, which, if the ordinary 10 per cent. bronze is used, are susceptible to self annealing, an alloy containing 7 per cent. aluminium, 3 per cent. iron, 1 per cent. manganese metal is suitable, and has a tensile strength of about 72,000 lb. per square nch with 40 per cent. elongation.

## Impact Hardness Testing.

THE measurement of ball hardness by impact methods is discussed by Dr. I. Class in *V. D. I.* for November 26th, 1927. The apparatus required for such methods has important advantages as regards size, weight, and general adaptability over the more cumbersome equipment required for the ordinary static Brinell test. The sketch, for instance, shows an




impact tester, devised by Dr. R. Baumann, which weighs scarcely 2 kilos. The anvil *a*, which carries the ball *b*, forms part of a central shaft acting as a guide for the hammer *c*. At the commencement of the test the hammer is pushed back against the compression spring *d*, until it is held by one of the hooks *f* or *i*. The ball is then pressed against the specimen and the collar *e* is pressed forward by hand until the automatic release *h* engages with the hooks, forces them open, and allows the hammer to fly back against

* U.S. Patent 1,264,459, 1918, was granted to C. Vickers in connection with the addition of iron to aluminium bronze in the proportion of not more than 5 per cent. nor less than 3 per cent.

the anvil. When the hook *i* is used the initial compression load in the spring at the moment of release is half that when the hook *f* is used, that is, the energy at impact is reduced in the ratio 1 to 4. In this manner the size of the impression can, to some extent, be controlled according to the hardness of the specimen. Further control can be obtained by altering the position of the sleeve carrying the hooks in relation to the compression spring. The instrument is used in the horizontal position, and it is important that the specimen and its support should have sufficient inertia to ensure that all the impact energy is used in forming the impression. Dr, Baumann states that the requisite masses are 5 kilos. and 20 kilos. when hooks *i* and *f* respectively are used.

In the static Brinell test the relation between the applied load P and the diameter of the impression is found to be

$$P = a\,d^n$$

where $a$ and $n$ are constants for a given ball diameter and material.

It will be seen that $a$ is the load necessary to produce a unit diameter impression, and therefore depends upon the ball diameter, whilst $n$ depends upon the material, having a value which usually lies between 2·0 and 2·5.

Experiments with the impact hardness tester show that a similar law, viz. :—

$$A = a_1\,d^{n_1}$$

holds between the work A absorbed in producing the impression and the diameter $d$. The constants $a_1$ and $n_1$ are, however, different from $a$ and $n$ of the static test ; $a_1$ is usually greater than $a$ and $n_1$ less than $n$. For the ferrous materials $n_1$ is found to have a value approximating very closely to 2.

Now from considerations of the static test, the work done $l$ per unit volume of impression can be calculated, and it is found that the ratio between $p$ and $l$ is, approximately,

$$\frac{p}{l} = \frac{n+2}{4}$$

where $p = P \Big/ \frac{\pi d^2}{4}$ = Static load per unit area of impression.

From this it is clear that if $n = 2$, as it appears to be for ferrous materials in the static test, $l$, the work per unit volume of impression, is independent of the total energy of impact, the ball diameter, and the diameter of the impression. The quantity $l$ can thus in these circumstances be used as a hardness number, and can be determined from a single test. If $n$ is not equal to 2, as in the case of non-ferrous materials, a constant value of the energy of impact must be maintained in order to obtain a comparative series of hardness numbers.

If Brinell numbers are required, a calibration of the impact tester can be performed to give curves connecting Brinell number and diameter of impression for the apparatus.

## The Heat of Mixture of Molten Metals.

A CONSIDERABLE number of investigations on the heat of mixing of organic liquids and of various salt solutions have been recorded, but owing presumably to the much greater experimental difficulties involved, data for the heat of mixing of molten metals are much scarcer. The problem has, however, recently been attacked by M. Kawakami, who has measured the heat of mixing of the potassium-sodium, mercury-tin, cadmium-lead, tin-zinc, bismuth-zinc, cadmium-zinc, lead-zinc, mercury-potassium, mercury-sodium, zinc-antimony and cadmium-magnesium systems.

Three types of apparatus were used. The first is shown in Fig. 1. It consists of a sheet iron vessel of elliptical cross section which serves as a thermostat and which contains the calorimeter. C is an iron stirrer. The thermostat is heated by means of a nichrome coil and contains a eutectic mixture of sodium and potassium nitrates. The calorimeter consists of an iron vessel A supported on alumina edges. The iron stirrer C is attached to an alumina

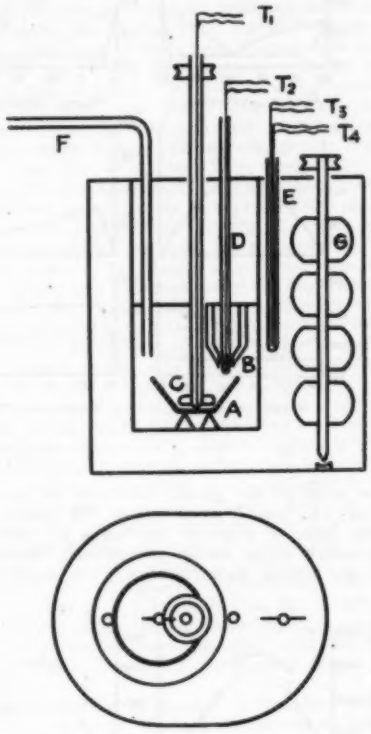



FIG. 1

tube, and at the bottom end of this and inside it is placed one junction of a copper constantan thermocouple $T_1$. D is an alumina tube, which carries a short iron rod at its lower end, and this can be screwed into the hole at the bottom of the vessel B. The method used is the method of mixtures. The two molten metals are held apart in the vessels A and B. When the whole apparatus has attained constant temperature, the rod in the end of B is removed and the metal flows from B into and mixes with that contained in A. It is, of course, extremely important to prevent any trace of oxidation, and this is done by passing through the apparatus a current of hydrogen, which is finally purified over sodium. The temperature difference between the two vessels A and B is measured with a differential thermocouple $T_1T_2$, and the temperature rise in A after the

two metals have been mixed is measured with the differential couple $T_1T_2$.

Some of the results obtained are shown graphically in Fig. 2, with the corresponding equilibrium diagrams. It will be seen that in cases where simple

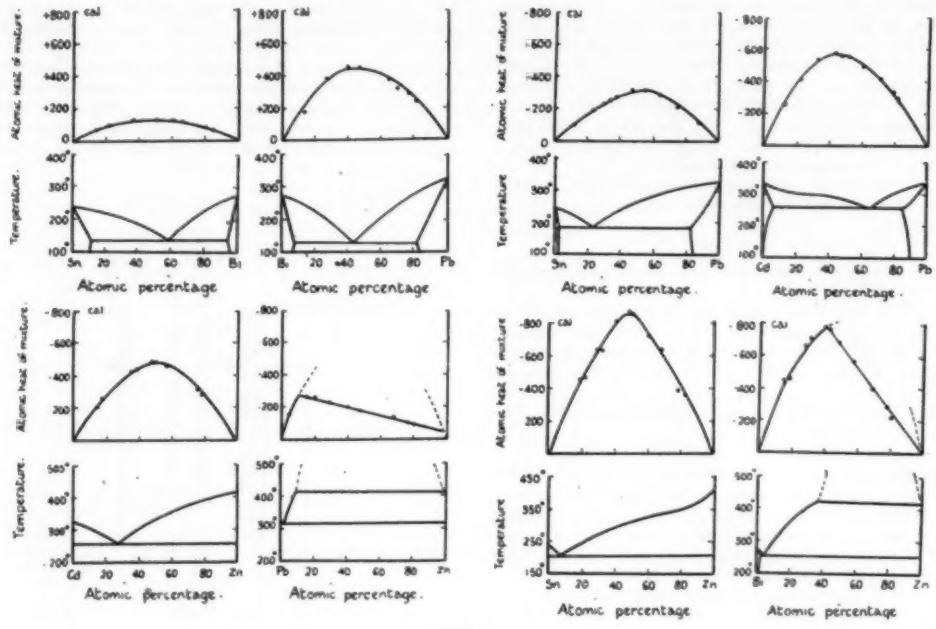



FIG. 2

eutectic systems are given, the heat of mixing is negative—i.e., heat is absorbed by the system—and that the heat of mixture reaches a maximum at approximately equal atomic percentage. Exceptions to this are certain bismuth alloys, i.e., bismuth-tin,

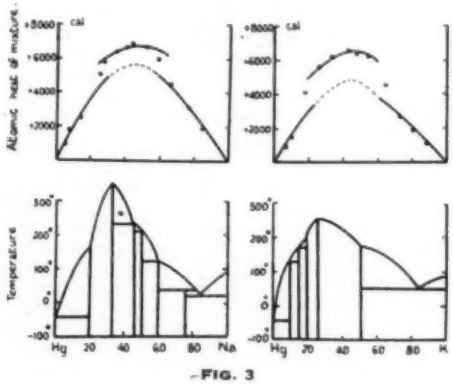



FIG. 3

bismuth-cadmium and bismuth-lead, where the heat is positive, but the maximum is again found at an equal atomic percentage. The bismuth-zinc and lead-zinc systems have at 450 deg. an immiscible region in the liquid phase, and in these alloys, as the ratio of the

two phases in the heterogeneous range will be a linear function of the percentages, the heat of mixture will vary in the same way. This was found to be the case.

In the second type of apparatus, the systems mercury-sodium, mercury-potassium, were examined. In these alloys there is a range of composition where, at the temperature of the experiments, the alloy consists either of a mixture of solid and liquid phases or is completely solid. In these cases the heat of mixing includes the heat of solidification. The lower

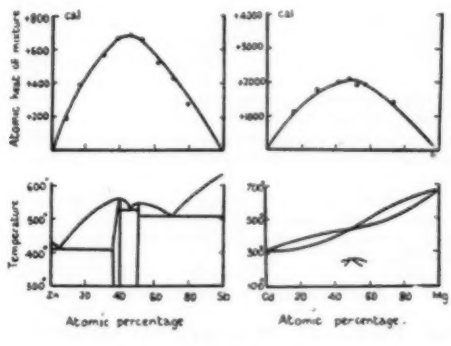



FIG. 4

curves—Fig. 3—show the heat of mixture, excluding the heat of solidification. Every alloy in these systems contains at least one compound, so that in these cases the heat of mixture includes the heat of combination. This is usually large and is positive,

and it is found in these two cases that the heat of mixture is positive, and about ten times greater than in the previous cases—simple eutectiferous systems. From these results, the important conclusion is drawn that an intermetallic compound is not decomposed on melting, but can exist as such in the liquid state.

In a third type of apparatus the systems zinc-antimony and cadmium-magnesium—systems which form intermetallic compounds—were investigated. The heat of mixture was found to be positive and to attain a maximum at approximately an equal atomic percentage of the component metals—Fig. 4.

## Recent Developments in Cast Iron

By J. G. PEARCE, B.Sc. (Eng.), M.I.E.E.

No. I.

AT one time the technical development of cast iron was stifled by the fear that any consequent increased cost of production would too far diminish its competitive margin over the steels and non-ferrous metals. It is now recognised that improved cast irons may not only find fields of application entirely their own, but may win back fields previously lost to competing materials, and during the past ten years a number of advances have been made from the metallurgical point of view.

Information on improved cast iron is invariably put before the inquirer in the form of test results. It must be admitted that in cast iron perhaps more than in any other cast metal, no test provides an ideal criterion of the casting itself. We may go further and say that no reasonably practicable combination of tests really affords such a criterion, and ultimately service experience is the only effective guide to behaviour. The designer is thus mainly enlightened by failure, and in ordinary cases the margin of safety employed is great because no undue risk of failure can be incurred. Service tests, however, take long periods to complete, and are often inconclusive, owing to the inevitable operation of undesired variables. We are thus forced back on laboratory test results, which, for reasons indicated below, require to be considered with caution.

Some foundries, especially those making big castings, do not make use of mechanical tests at all, but use a chill test as a convenient means of ascertaining those influences of composition and rate of cooling which affect the final structure, while the mass of the metal is still fluid. In many foundries the test suggested by Keep is still used, a half-inch square bar, 12in. long, being cast in a yoke. The shrinkage of this bar is used as an index of silicon content, and this is a tolerably reliable guide, provided that working conditions are reasonably constant. Variations in total carbon and sulphur, however, may cause unexpected changes in shrinkage, although practical experience and auxiliary indications afforded by the transverse strength of the bar, the fracture, and depth of chill at one chilled end, provide additional data from which reasonably accurate deductions may be drawn.

The transverse test is by far the most popular strength test in the foundry, for the bar is easy to cast and can be tested without machining. The breaking load and deflection figures are easily understood, and both are usually specified—by the Admiralty on a 1in. square bar on 12in. centres, and by the B.E.S.A. on a 2in. by 1in. bar on 36in. centres. The familiarity of engineers with the tensile test on steel has resulted in recent years in a pronounced tendency to specify this test for cast iron, either in addition to the transverse test or as an alternative, although it is not popular in the foundry. It requires machining, and the tensile testing machine is more elaborate and costly than a simple transverse machine. Cast iron is also very sensitive to non-axial loads. Shoulder breaks on tensile pieces are common when this fault is present, and the results are accordingly erroneous.

Assuming agreement as to the desirability of the transverse and/or the tensile test, should the test bar be cast separately or as part of the casting? Save in the case of defective castings, and in certain special large and important pieces having excess metal in the form of big risers, it cannot be actually cut from the body of the metal. Bars forming part of the casting—"cast-on"—are favoured by inspectors, who are thus afforded an implicit guarantee that the bar was cast at the same time from the same metal, but metallurgically the separately cast bar—"cast-off"—is preferable. In a casting of varying section, no single bar, cast-on or cast-off, can be said truly to represent the casting as a whole. In the cast-on bar this difficulty is complicated by the influence on the attached bar of the rate of cooling of the mass. This varies with the size of the casting and the situation of the bar with respect to it, and any strict comparison between different bars is impossible. The most logical plan is therefore to cast a bar separately, of the same metal and at the same time, thereby eliminating variations of this kind. The size of the bar chosen should be related to the size of the casting. Otherwise, a large casting of hard metal might be represented by a white or mottled bar. Conversely, a thin casting is unfairly represented by a slowly cooled test bar of heavy section. The relationship is complicated by practical considerations. A very heavy test bar cannot be tested by machines ordinarily available, while it is not practicable to cast test bars below a certain thickness. In many castings variations in section will make a very precise relationship impossible. If the section of a separately cast bar is related to the thickness of the casting represented, it may fairly be said to represent more than the metal put into the casting, while comparison between different bars is possible.

If developments in the art of founding are communicated in terms of specific mechanical tests, the bearing of these preliminary remarks will be appreciated. How often do these test results specify whether the bar is cast-on, cast-off, or cut from a casting, or the size of the original section from which the bar was machined? Without some indication of the location in and size of the section from which bars are taken, the results of tensile and transverse tests are difficult to gauge, and others, such as Brinell hardness and combined carbon content, are meaningless.

Compared with that of steel, the ductility of cast iron is negligibly small, but even within so narrow a range there are degrees of ductility where cast iron is concerned, some irons being extremely brittle, while others have a measure of toughness. The latter are, of course, to be preferred, although they may have a lower tensile strength than the brittle irons. A tensile test alone may therefore be very misleading. Elongation figures given in tests for

cast iron obtained otherwise than with an extensometer should be accepted with reserve, as the difficulty of securing perfect registration of broken parts will always result in showing some degree of elongation when measured over the gauge length.

The repeated impact test on a Stanton type test piece has been used for differentiating empirically between brittle and tough irons, although this test, like some others, suffers from the smallness of the test piece and the fact that its size is not varied with the size of the casting represented.

Recent Wohler fatigue tests[1] have shown cast iron in an unexpectedly favourable light with respect to endurance ratio (ratio of stress limit at which material is capable of withstanding an infinite number of reversals to the ultimate tensile strength), to its response to understressing (which increass the endurance limit by 30 per cent.), and to the relative ineffectiveness of "stress-raisers," like holes and grooves, in lowering fatigue strength.

The mechanical properties of cast iron are determined by its structure, which, in turn, is governed by two factors, composition and rate of cooling, the influence of which cannot be wholly separated. The composition factor itself includes the effect of total carbon, silicon, manganese, sulphur and phosphorus and in alloy cast irons several further elements. The rate of cooling is governed principally by pouring temperature, mould temperature, and casting section. Many changes can thus be rung in trying to secure a particular result. The metallurgist generally aims at a homogeneous structure of pearlite broken up by a minimum of well-distributed graphitic flakes and phosphide areas of small size. Maurer has endeavoured to show diagrammatically from actual test results with silicon as abscissæ and total carbon as ordinates, after the manner of Guillet's diagrams for steel, that the pearlitic structure will be confined to a particular triangular area, the region to the left showing white and mottled and the region to the right showing ferritic iron.[2]

The limitations of a two-dimensional diagram in dealing with so many variables are evident, for it ignores the influence of other elements of composition and of thickness, although the idea has recently been extended to indicate the range of thickness in which pearlite is obtained.[3]

Greiner and Klingenstein[4] endeavoured to introduce both factors by means of a diagram defining pearlitic irons with total carbon + silicon as ordinates and casting thickness as abscissæ, but this presumes that in the sum of total carbon and silicon a diminution of one element may be compensated by an increase of equal amount in the other. This is only a rough first approximation, and from chilling experiments is known to be incorrect.

Any attempt at improvement naturally seeks, first, to reduce interruptions of the basic structure by diminishing phosphorus and free graphite, and to secure the graphite in a finely divided state. Secondly, the matrix is made more homogeneous by rendering it wholly pearlitic, which requires the maximum amount of carbon in the combined form consistent with free machining properties, and hence—for a given total carbon—leaves a minimum of graphite. This involves a lower silicon than is used in ordinary irons, which in turn necessitates the use of low-silicon pig irons relatively high in manganese to ensure the bulk of the sulphur being present as manganese sulphide. The precise composition employed is determined with regard to the thickness of the casting and the foundry procedure to be adopted, but it must be emphasised that it is more important to produce a sound casting free from gas and air cavities and from internal stress than to produce a casting that, although represented by a test piece relatively high in tensile strength, is not necessarily sound and tough. The limits of castability are easily overstepped. Total carbon and phosphorus may be reduced to a point at which the difficulties associated with steel casting will be encountered. Thus there is a practical limit for what may appear to be metallurgically desirable compositions, and this is determined by experience.

[1] Univ. of Illinois, Bull, No. 164, "Tests of the Fatigue Strength of Cast Iron," by Moore, Lyon and Inglis, and THE METALLURGIST, December, 1927, page 188.

[2] Maurer, *Kruppsche Monatshefte*, July, 1924, 5.115; *Stahl und Eisen*, 1924, 44.1523.

[3] Maurer and Holtzhaussen, *Stahl und Eisen*, October 27th, 1927, 47.1805, and November 24th, 1927, 47.1977.

[4] *Gusseisen-Taschenbuch*, 1926, page 13, and British patent 260,990.

## The Alloys of Chromium and Iron.

SINCE 1907 when Treitschke and Tammann[1] attempted to establish the chromium-iron equilibrium diagram a number of attacks have been made on this system in Germany. Most recent is the work of Oberhoffer and Esser—December, 1927[2]—who, with the aid of X-ray examination, have endeavoured to rectify the somewhat tentative conclusions of the earlier work of Pakulla and Oberhoffer—1925.[3] The two latter publications are best considered together, since one is really the supplement to the other. In their review of previous work the authors refer to the slowly forming compound "X," which was assumed in order to explain the unusual type of diagram given by Treitschke and Tammann. Later, Monnartz—1911[4]—and Janecke—1917[5]—produced diagrams differing from each other and from that of Treitschke and Tammann, the discrepancies being attributed by Fischbeck to the presence of carbon. Pakulla and Oberhoffer also point out that the steady fall of the $A_2$ transition point with increasing chromium content, found by Murakami, suggests complete mutual solubility of the two metals in the solid state. The real explanation of the discordant results obtained by the early workers, however, is that their alloys were contaminated with nitrogen rather than carbon. Investigation at the National Physical Laboratory[6] has recently shown that nitrogen is rapidly absorbed by chromium and chromium iron alloys at elevated temperatures, and gives rise to structures similar to those generally attributed to the presence of carbon.

The investigations made at Aachen were conducted on alloys made up with vacuum melted electrodeposited iron and "thermit" chromium. Both the samples of chromium used contained over 1 per cent.

[1] Treitschke and Tammann, *Z. Anorg Chem.*, 55, 1907, page 402.

[2] Oberhoffer and Esser, *Stahl und Eisen*, Nr. 48, December 1st, 1927.

[3] Pakulla and Oberhoffer, *Berichte Werkstoffausschluss v.d. Eisenhuttenleute*, Nr. 68, 1925.

[4] Monnartz, *Metallurgie*, 8, 1911, page 161.

[5] Jänecke, *Zeit. Elektrochem*, 23, 1917, page 49.

[6] Adcock, *J.* of Iron and Steel Inst., 1926, II., 117.

of impurities other than iron. Consequently, it is difficult to share the authors' conclusion that the chromium-iron diagram may now be regarded as settled—since a displacement of the equilibrium lines is probable in the presence of appreciable amounts of silicon or aluminium. A brief description is first given of introductory work conducted in a furnace of the carbon-resistor type—a record of great difficulties in connection with refractories and thermo-couples. The melts rapidly attacked the couple-protecting sheaths, and even in cases where a complete break through did not take place, the couple wires were often contaminated with gases. Since the thermal results could not be reconciled with the micro-structures of the alloys, the authors consider that carbon absorbed by the alloys from the furnace gases had caused a breaking down of the solid solutions.

After an extensive preliminary research, a molybdenum wound furnace was perfected, the melting operation being conducted in an atmosphere of carefully purified hydrogen. Some oxidation of the melts still occurred, however, even under these conditions, the oxygen being apparently derived from refractories containing silicon, which was reduced in the presence of the metal. De-oxidation of the alloys by means of magnesium was not entirely successful, and the metal showed the presence of some impurities; on the whole, however, micro-structures were suggestive of solid solutions.

Finally, the alloys were prepared in a molybdenum-wound furnace operated under vacuum conditions, a process which involved special difficulties, owing to the pronounced vaporisation of the metal and refractories at high temperatures. Magnesia crucibles had to be discarded owing to their rapid destruction by the melts, and ultimately were replaced by crucibles of technically pure alumina, which contained about 5 per cent. of silica. The melts weighed about 100 grammes, and it was found essential to introduce the intimately mixed components in a finely divided state, and to hold high chromium alloys at 1700 deg. Cent. for 50 minutes to obtain homogeneity. All the fifteen alloys examined microscopically indicated solid solutions, but the authors do not record the micro-structures of any alloy between 2·28 per cent. and 10·38 per cent. Cr, a very important range. In order to avoid the attack on the thermo-couple wires by metallic vapours at temperatures over 1200 deg. Cent., the thermal evidence was secured by means of an "Ardometer," which is essentially a total radiation optical pyrometer fitted with a recording device. The published curves are not as definite and convincing as one would wish, but allowance must be made for the extraordinary difficulties, which practically preclude the use of thermo-couples. For example, the authors found it impossible to obtain a proper melt of chromium in the furnace, although a temperature of 1700 deg. Cent. was attained; the metal evaporated and penetrated the crucibles, leaving only a few isolated globules. Six alloys ranging in composition from 2·28 per cent. to 29·18 per cent. chromium were investigated in the solid state by means of a sensitive dilatometer.

Fig. 1 shows the chromium iron diagram as established by Pakulla and Oberhoffer in 1925, the outstanding feature being the continual fall of both $A_3$ and $A_2$ with increasing chromium, and the merging of the $A_3$ and $A_2$ equilibrium lines for compositions over 20 per cent. chromium. The liquidus indicated a minimum between 10 and 15 per cent. chromium, with a sharp rise on the chromium side. Apparently, the $A_4$ arrest was not investigated.

A hardness table of the chromium-iron alloys is also given. Although the hardness of chromium was not actually obtained, owing to brittleness of the metal, the dotted extension of the hardness curve for the alloys indicates a value of about 360 Brinell for chromium. This appears to be very high, since the hardness of properly treated electro-deposited chromium prepared at the National Physical Laboratory did not exceed 114 Brinell, while even samples of commercial "Thermit" chromium fall below a figure of 170.

The later research on the chromium-iron diagram by Oberhoffer and Esser was undertaken chiefly to

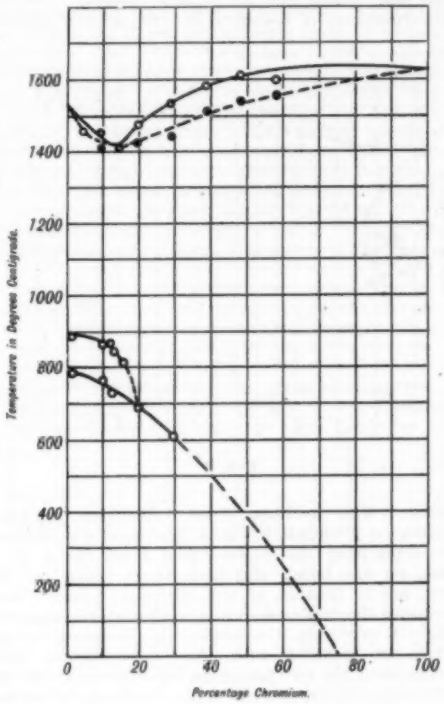



FIG. 1

ascertain whether a compound exists in the system, and to reinvestigate, in particular, the equilibrium conditions of the lower percentage chromium alloys in the solid state. The diagram, as determined by Pakulla and Oberhoffer, indicated that all alloys containing over 20 per cent. of chromium should consist of the $\gamma$ iron phase, and since X-ray evidence was not in harmony with this requirement, the actual course of the $A_3$ equilibrium line became open to question. As in the previous research, the alloys were prepared in 100-gramme melts in a molybdenum vacuum furnace. X-ray exposures were then secured with specimens ranging in composition from 0·50 to 29·18 per cent. Cr, up to 1000 deg. Cent. A rather serious gap extending from 0·55 to 10·38 per cent. chromium occurred in the alloys utilised for the purpose. This range of composition was, however,

adequately covered by thermal observations obtained by the differential method—nickel neutral body—made in an evacuated "Silit" furnace capable of reaching temperatures of 1300 deg. Cent. The thermal arrests—for the solid alloys—became less pronounced and more difficult to determine in the region over 10 per cent. chromium, and it was in the composition range of, say, 8–20 per cent. chromium that the X-ray investigation yielded valuable and decisive evidence.

As will be seen from the diagram evolved by Oberhoffer and Esser—Fig. 2—the $A_4$ transition line falls with increasing chromium content, ultimately becoming vertical and meeting the line of the $A_3$ arrest. The latter falls at first with increasing chromium, but rises again after reaching a minimum at about 8 per cent. chromium. The isolated "$\gamma$" phase field which extends to approximately 14 per cent. chromium is bounded by two narrow duplex

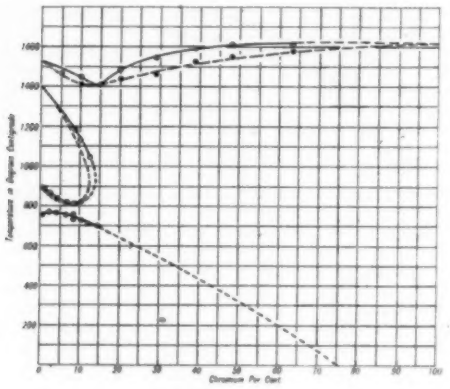


FIG. 2

regions. The authors point out from thermodynamic considerations that the two equilibrium lines separating the duplex field from the $\alpha$ or $\delta$ phase, on one hand, and from the $\gamma$ phase on the other, are in contact at the minimum point. This eliminates the duplex field at a composition—approximately 8 per cent. Cr—where the tangents to the curves are parallel with the concentration axis. At this point the two phases in equilibrium are of the same composition. On the other hand, at the border of the $\gamma$ field at compositions near 14 per cent. chromium, the tangents to the equilibrium lines are vertical to the axis of concentration. Here the $\alpha$—or $\delta$—and the $\gamma$ phases in equilibrium are not of the same composition.

No evidence of the existence of a compound was obtained, and the authors conclude that chromium and iron form a continuous range of solid solutions. In the diagram—Fig. 2—the $A_2$ equilibrium line, after a very slight rise, falls steadily and reaches room temperature at a composition of about 75 per cent. Cr. The differences in shape between the $Ar_2$ and $Ac_2$ and also the $Ar_2$ and $Ar_3$ thermal arrests obtained by the differential method attracted the attention of the authors, who were of the opinion that the heat evolution or absorption associated with $A_2$ takes place over a temperature range and not at constant temperature.

A valuable description is also given of an automatic temperature regulator used by the authors for controlling the furnace which was employed during the recording of the differential thermal curves. Given adequate supplies of electrolyte, &c., the apparatus is capable of raising and lowering the temperature of the furnace steadily at the required speeds over a definite temperature range. The reversals which take place at the maximum and minimum furnace temperatures were also effected automatically, and, if desired, the process of alternate heating and cooling could be maintained indefinitely.

The great advance made by Oberhoffer, Pakulla and Esser in the knowledge of the chromium-iron system is to be attributed largely to their perfection of the technique of high-temperature melting under vacuum conditions. The practical difficulties connected with the preparation of their alloys were formidable, but the labours of the investigators in overcoming them were well repaid, the greater purity of their specimens saving them from the pitfalls and conflicting experimental results which beset the earlier researches.

## Normal and Shear Stress in the Testing of Materials.*

IT is known that a tensile load applied in a given direction to a specimen of any material gives rise to a tensile stress in the direction of the load and a pair of shear stresses at 45 deg. to this direction. In a homogeneous isotropic material failure can thus occur in one of two ways. If the natural resistance of the material to shear is large compared with its resistance to molecular separation—that is, its cohesion—the specimen will fail in tension as soon as the tensile stress exceeds the cohesion, before any deformation begins. The specimen appears to be brittle. If, on the other hand, the shear resistance is small in relation to the cohesion, permanent distortion will occur as soon as the shear stress exceeds this resistance. In this case the material is said to be ductile. The mechanism is very similar in a material composed of a crystalline aggregate. For practical purposes, particularly, if its structure is fine grained, such a material can be regarded as virtually isotropic. The shear resistance will, however, be considerably higher than that of the individual crystals, since, as will be easily understood, these mutually strengthen one another.

The usual method of presenting the results of tensile tests—viz., plotting normal stress against extension—does not bring out clearly the relation between cohesion and shear resistance. The latter is determined by the stress at the yield point, but the former is not given by the ultimate tensile strength. A clearer conception is obtained by plotting the true mean stress, that is the applied load at any instant divided by the corresponding area at the minimum section against the ratio $\frac{\text{reduction of area}}{\text{original area}}$. Such a curve is shown in Fig. 1. The stress at the point A corresponds to the maximum ordinate of the nominal stress extension curve; that is to the stress usually termed the ultimate strength; whilst the true mean breaking stress is given by the stress B $b$. At this value of the stress the cohesion of the material is over-

* From a lecture by P. Ludwik to the German Society for the Testing of Materials, October 27th, 1927. See also *V.D.I.*, October 29th, 1927.

come and fracture commences at the axis of the specimen where the stress is a maximum. This mean breaking stress approaches much more nearly to the cohesive strength of the material than does the ultimate strength. Moellendorff and Czochralski have, in fact, found that after the commencement of "necking" the true mean tensile stress $\sigma$ increases at a rate approximately proportional to the reduction of area $\psi$—Fig. 1—and tends towards a limiting value

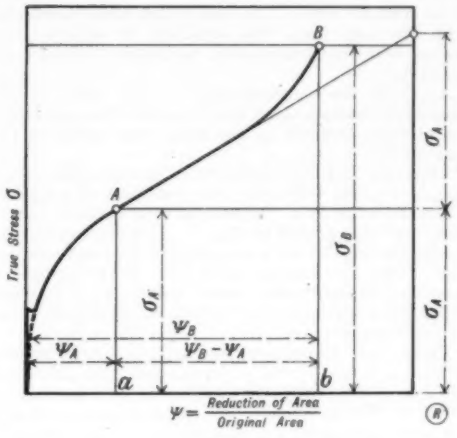



FIG. 1

$\sigma = 2\sigma_A$, when $\psi = 1$. Hence, the true mean maximum tensile strength can be approximately calculated from a knowledge of the true stress, which is equivalent to the ultimate tensile strength, and the values of $\psi_A$ and $\psi_B$— that is, the uniform extension and the reduction of area at fracture.† It should be noted that the mean maximum tensile stress thus obtained from tensile tests is not a definite physical quantity, since it will depend on the distribution of stress across the minimum section, which itself depends upon the contraction of area. Moreover, it will not necessarily represent the true tensile strength of the material in its original condition, since this may be altered by the deformation incurred during the test. It is important also to notice that there is no relation between the ultimate tensile strength and the mean maximum tensile stress. The former is a measure of shear resistance in ductile materials, whilst the latter is an indication of the cohesion. By appropriate treatment these two properties of a material can be varied independently of one another.

In all indentation hardness tests a shear resistance is measured so that a relationship between tensile strength and hardness is to be expected. In the zone of material affected by the test the metal is stressed above the shear limit, and since the resistance to shear is found to increase with the rate of deformation, it follows that the sharper the impression the higher the resistance to shear and therefore the higher the hardness number. From the geometry of the cone hardness test it is clear that the shear resistance will remain constant during the formation of the impression, irrespective of the depth, so that the hardness number expressed in terms of the area of the impression will be constant, and the load will vary with $d^2$, where $d$ is the diameter of the impression. In the ball test, on the other hand, the load varies as a power ($n$) of $d$ higher than 2, approaching the lower limit of 2 more closely the less the shear resistance increases with the rate of shear; that is, therefore, the flatter the load-extension curve of the tensile test. It is for this reason that $n$ is less for materials in the cold worked state that when annealed.

Shear resistance and cohesion are differently affected by alternating stresses. Under static tension failure occurs when the shear resistance has increased as a result of cold-hardening to such an extent that the tension necessary to overcome this increased resistance to shear exceeds the cohesion. It would seem that all the inter-molecular adhesions at the section of fracture are then almost simultaneously broken. In alternating stress, on the other hand, there is some indication that when the fatigue limit is exceeded, internal displacement of the structure of the material occurs at each reversal, in such a manner that by degrees more and more adhesions are severed. It appears, therefore, that fatigue failure occurs as a result of a progressive loosening of the crystal lattice, and is associated with a decrease in cohesive strength.

So far only uni-axial stress has been considered, and it is necessary to discuss now the effect of three-dimensional stresses, which is found to have an important bearing on the behaviour of materials under

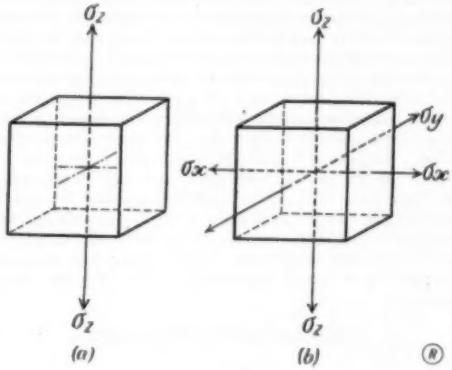



FIG. 2

certain types of loading. In a cube of material, stressed as in Fig. 2A, the maximum shear stress S is equal to $\frac{1}{2}\sigma_z$, whereas for the case of three-dimensional loading, shown in Fig. 2B, it is equal to $\frac{1}{2}(\sigma_z - \sigma_x)$, if $\sigma_y$ is assumed equal to $\sigma_z$. It is thus clear that in this condition the more nearly the principal stresses approach one another in magnitude, the greater will be the tensile stresses necessary to produce shear stresses equal to the shear resistance of the material. If these tensile stresses are sufficient anywhere to overcome the local cohesion, fracture will occur, and if, further, the limit of shear resistance has not yet been reached, the fracture will be unaccompanied by any permanent distortion. It is thus possible for materials exhibiting pronounced ductility under ordinary tensile tests to become quite brittle when subjected to three-dimensional stress. This fact has an important bearing on notched bar impact testing, since, according to R. Baumann, the

† See also THE METALLURGIST, October, 1927, page 149, "Local and Uniform Extension in the Tensile Test."

action of the notch hinders the free flow of the material and thus gives rise to a state of three-dimensional stress.

This reduction of ductility in the notched bar test is further emphasised by a similar effect due to the rise of shear resistance with rate of deformation—a feature to which passing reference has already been made. This phenomenon is well illustrated by zinc. A thin rod of this material can be easily bent slowly to almost any desired degree, since the shear resistance is then low; but under rapid bending the rod will break at once, since the shear resistance reaches such a value that the tensile stress necessary to overcome it exceeds the cohesion. Effects of this kind are particularly marked in notched bar impact tests, where the deformation that occurs is severely localised in the region of the notch. As a consequence, even at low impact velocities the rate of shear must be rapid in that region, and a pronounced increase in shear resistance arises. It is for this reason that many otherwise ductile materials exhibit brittleness when tested by the notched bar impact method.

Heat treatment is a powerful factor in modifying the impact strength, acting, it would seem, by altering the relative magnitudes of the cohesion and shear resistance. A large drop in impact strength will always occur when the ratio of the cohesion to the shear strength falls below a certain limiting value, as a result of either an increase in shear resistance or a decrease in cohesive strength. The magnitude of this limiting value will depend upon the material, the impact velocity and the conditions of stressing. Implied in the latter variable are also the shape of notch and width of test piece. It appears therefore that too high a shear resistance, as evidenced by too high a dynamic elastic limit, may be undesirable from the standpoint of power of withstanding suddenly applied loads. On the other hand, a high resistance to shear is desirable for most service conditions, particularly for high endurance to alternating stress. High impact strength and high endurance can therefore only be obtained together by maintaining the shear resistance and increasing the cohesion. The latter can be very materially increased by normalising, a process which raises the cohesive strength by a larger amount than it does the shear resistance.

## Allotropic Changes in Tin and Lead Alloys.

IT is well known that in the alloys used in the printing industry containing tin, lead and antimony, changes occur even at the ordinary temperature. Immediately after casting, the alloys are harder and less dense than they are after remaining at room temperature for some time; softening and increase in density take place. These and allied phenomena have been studied by Messrs. Travers and Houst, who describe their work in the *Revue de Metallurgie* for September, 1927.

In order to investigate the changes which take place in these alloys, a dilatometric method was used. Briefly, this consisted in measuring the length of a bar of the metal at various temperatures. It was found that it was necessary to maintain the specimen at any temperature at which a measurement was to be taken for a prolonged period, because even after a constant temperature had been attained, the length of the bar continued to change until equilibrium at that temperature had been established. The limiting length was measured in each case.

It was found that in the case of Monotype alloy the maximum contraction—$17 \times 10^{-3}$—occurred at 210 deg. Cent. after 178 hours, but it may be pointed out that such contraction would have occurred at a lower temperature had the time of annealing been sufficiently prolonged. With increasing tin content the limiting contraction increased, but varying the amount of antimony present in the alloy was found to be without effect. It was found that quenching from 180 deg. Cent. was sufficient to suppress the change and that subsequent annealing caused contraction.

Applying the same method to the study of the binary system lead-tin, it was found that the maximum contraction occurred in the alloy containing 16 per cent. of tin.

*Allotropy in Lead.*—Dilatation measurements on a sample of lead indicated the presence of two discontinuities in the expansion-temperature curve. These are reproduced in Fig. 1. It will be seen that the discontinuities occur at about 60 deg. and 180 deg. Cent. The two breaks occur only if the sample is examined immediately after solidification; eight hours after solidification, only one discontinuity at 60 deg. Cent. is found.

These two discontinuities suggest three varieties of lead $\alpha$, $\beta$ and $\gamma$, the $\gamma$ variety being stable above 180 deg. Cent. Ordinary lead would be a mixture of $\alpha$ and $\beta$. The passage of one variety into another is not accompanied by an expansion or contraction, and the only dilatometric indication is a change in direction of the length-temperature curve.

*Allotropy in Tin.*—Two well-marked varieties of tin are known—ordinary white tin and grey tin. The former is obtained by normal cooling from the liquid and also by electrolytic deposition. It has a density of 7·28 and crystallises in the tetragonal system. Grey tin is stable at temperatures below 18 deg. Cent. According to the authors, it is "amorphous," and has a density of 5·79. This has been studied by Cohen.[1]

About 1880 Trenchman and Foulton discovered a third modification which can be formed when molten tin is exceedingly slowly cooled. This form of tin crystallises in the rhombic system and is brittle. According to Trenchmann it has a density of between 6·52 and 6·55 at 15 deg. Cent., but the specimen studied was not pure.

The difference in density between the tetragonal and rhombic forms of tin led Cohen and Goldschmidt[2] to determine the temperature of transition of one form into another by a dilatometric method. However, no indication of a point of transition was discovered.

Degens attempted to determine the transition point using a dilatometric method. As dilatometric fluid, a volume of air retained by a volume of mercury was employed. In this way errors due to decomposition of the oil of the dilatometer were overcome. Degens found by this method that a transition point occurred at a temperature of 161 deg. Cent.

Repeating the work of Degens, A. Smits and H. L. de Leeun[3] found that using the same method as Degens, the existence of a transition point could be established, but that in successive experiments the

[1] Cohen, *Z. Phys. Chem.* (1899), XXX., 601; (1900), XXXIII., 57; XXXV, 588; (1901), XXXVI., 514; (1904), IXLVIII., 243; (1905), L., 225; (1908), LXIII., 625.

[2] Cohen and Goldschmidt, *Z. f. Phys. Chem.*, 50, 1904.

temperature at which the transition occurred became lower and lower, and that, on analysis, the tin was found to contain mercury. Further investigation showed that mercury acts as a catalyst, causing the transition of rhombic to tetragonal tin to occur in a much shorter time. The temperature of the transition is also lowered considerably by the presence of mercury. Smit and Leeun found the temperature of the transition to be 202·8 deg. Cent.

Werner[4] has studied the question from two points of view—(*a*) pressure-temperature; (*b*) electrical conductivity as a function of the temperature. In one instance—Fig. 2—Werner obtained a discontinuity in the pressure-temperature curve at a temperature of 168 deg. Cent. and a pressure of 100 kilos. per square centimetre. He adds that when he repeated the experiment for the same pressure he did not find a discontinuity.

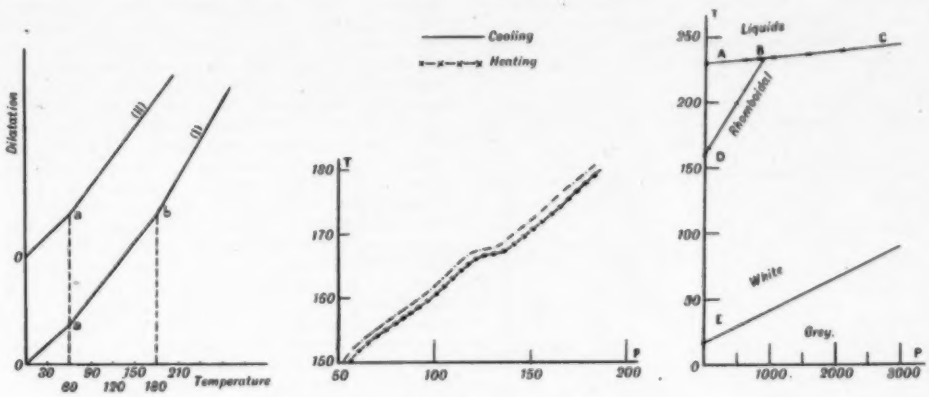
Although these results are for the most part negative, Travers and Houst have not hesitated to rely on the work of Degens and that of Tamman[5] on the flow of the metal under pressure. According to the latter author, the rate of flow of tin undergoes a discontinuity for a pressure of 50 kilos. per square centimetre at a temperature of 203 deg. Cent. Degens has found $t_{trans} = 161$ deg. Cent. for a pressure of 1 kilo. Werner, as stated, found $t_{trans} = 168$ deg. Cent. for $p = 100$ kilos. per square centimetre.

These three points lie on a straight line—Fig. 3. From this line we can calculate the value of $dp/dt$, which is found to be 0·084, and from Clapeyron's formula it is possible to find the variation in volume accompanying the change.

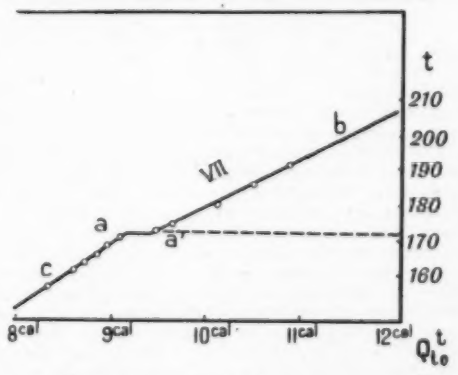
$$U_{\text{Sn quad}} - V_{\text{Sn rhombic}} = 0{\cdot}00017 \text{ grammes per cubic centimetre.}$$

Werner's curve, reproduced above, is interesting, but is not of much importance, since it is based on one result, which Werner was unable to repeat. Werner's experiments on the electrical conductivity did not lead to any conclusive result, since the discontinuity observed was of the same order as the experimental error.

*Calorimetric Method.*—This method, as used by Travers and Houst, consists in determining the total heat of a specimen of tin at various temperatures. The specimen, weighing about 40 grammes, is heated in a specially constructed furnace to the required temperature and is then transferred into a Berthelot calorimeter of known water equivalent. From the rise in temperature of the calorimeter, the total heat at the temperature, viz., $Q'_{t_0}$ is calculated. By plotting $Q'_t$, against temperature $t$, a curve is obtained. Curiously enough, the results depend to a great extent on the previous history of the metal. For instance, in the case of a sample which had been kept molten at 350 deg. Cent. for five minutes before




FIGS. 1 TO 3




Calorimetric curves for samples of tin superheated or not in the liquid state and cooled slowly or quickly.

*Curve* 1.—Melting temperature 350 deg. Cent., duration of melting, 5 min.; cast in iron moulds.

*Curve* 2.—Melting temperature, 350 deg. Cent.; duration of melting, 5 min.; cast in brine — 10 deg.

*Curve* 3.—Melting temperature, 500 deg. Cent.; duration of melting, 2 h.; slow cooling, 5 h.

*Curve* 4.—Melting temperature, 500 deg. Cent.; duration of melting, 47 h.; cast in iron moulds.

FIG. 4

casting, no discontinuity was observed in the $Q'_{t_0}/t$ curve, but, as will be seen from Fig. 4, slight discontinuities occur at a temperature of 172 deg. Cent. in samples which have been kept molten at 500 deg. Cent. for 5 hours and 47 hours respectively. Keeping

[3] Smit and Leeun, "Proc.," Amsterdam Acad., Vol. 14, 1912.
[4] Werner, *Z. Anorgan. Chem.*, 1913, LXXXIII., page 294.
[5] Tamman, *Domdes. Ann.*, X. (1903), 647.

the metal molten at 800 deg. Cent. for 47 hours gives a still greater break, as shown in Fig. 5.

From these results, the authors deduce the existence of two allotropic modifications of tin which persist in the liquid state, the change of one into the other occurring very slowly even at temperatures well above the melting point. Allotropic modifications of an element, even in the liquid state, are already known. Gerrez[4] has shown that the rate of crystallisation of sulphur is dependent on the temperature to which the liquid sulphur has previously been heated, and on the time it has remained at that temperature.

This hypothesis explains the anomalous results obtained by Werner and Degens, who would have

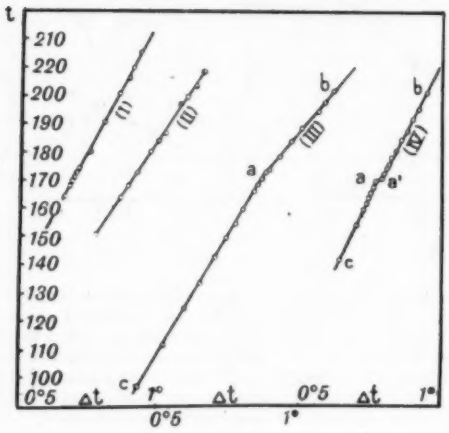



FIG. 5

obtained more consistent results had the previous treatment of the metal in the liquid state and the casting conditions been more uniform.

The authors do not refer to the work of Smit and Leeun[3] who had previously shown that partial transformation of tetragonal to rhombic tin can be produced by annealing tetragonal at temperatures above 200 deg. Cent. The change is slow, but is accompanied by a marked expansion.

From the abnormal course of the heating curve of tin in the region of the melting point, Smit concluded that at these temperatures tin behaves as a pseudo-binary substance, *i.e.*, it consists of more than one kind of molecule and that even before melting one form gradually passes into the other with absorption of heat.

## Forging Methods.

IN *The Drop Forger* for November, 1927, Mr. R. W Peck gives an interesting account of modern forging methods with regard to inspection and "progress." The Inspection Department is one of the most recent developments in a works, and requires careful organisation as well as tact and skill in those concerned.

In the first place the department undertakes the inspection of all raw materials for visible defects before any work is done on them. This external examination is highly important, as the raw materials may have passed all the laboratory tests and yet be unsuitable for high-class forgings. The rejected bars are not all sent back to the steel makers, but are graded. The first grade contains only the soundest materials which may be used for the manufacture of important forgings, such as front axles, crank shafts, connecting rods, &c. Second grade material is used for slightly less vital parts, such as gears. Third grade material is suitable for parts of still less importance, and the fourth for parts of least importance. The cost of this preliminary inspection works out at about £1 per ton for large billets and £2 per ton for smaller billets, as men soon become expert at the work.

Inspection of the actual forgings is the next task of the department. The Progress Section collects the forgings from the hammers twice per shift and delivers them to the pickling shop or sand blast so that they are ready for inspection next morning, and by noon the night shift work is also ready. It may be noted here that all viewing is carried out by day only. After inspection the progress staff moves the forgings to the heat treatment shop, whence they are again brought for further inspection. As the machine shops require the forgings to be free from scale and dirt, they are cleaned, and this process serves the purpose of a second view. A final view to eliminate any faulty pieces which may have escaped detection in the previous examinations is made before the forgings pass into the stores.

The above procedure ensures that inspection is carried out right from the raw material to the finished product, so that a minimum loss of time and material is incurred. Only sound forgings are submitted to heat treatment, and bad work is at once stopped and defects in stamping are quickly remedied. This system has led to a large reduction in the amount of forgings scrapped. For example, 30 to 40 per cent. stampers' scrap due to faulty raw material has been practically eliminated since the inspection of raw material has been in force. The viewing of stampings after pickling or sand blasting and before heat treatment is another innovation which saves much waste both in time and material.

Inspection must be undertaken with great care. The closer and stricter the examination of the raw material the less trouble there will be in the forge and in the later stages. It is very important that all the batches are carefully ticketed so that stampings are not mixed. In forges where the work is all cold clipped a necessary delay occurs before the stampings reach the viewer, but if the shop is properly organised, the work kept well in hand and each man's work trimmed and viewed separately, this delay is minimised.

Where cold trimming is employed and only small lots are made, inspection becomes more difficult, but a good method is to survey all the forgings at the end of each day as they are collected.

The author concludes his paper with some hints on the arrangement of forging or stamping shops. He advocates one or two rows of hammers only, running the length of the shop and with a good gangway to facilitate the removal of forgings. All counting of the stampings should be done by the progress staff. The inspection department should be situated between the stamping shop and the heat treatment department, and the whole connected by a light railway.

[4] Gerrez, *Comptes. Rendus.*, LXXXXVI. (1993), 1883: LXXXXVII. (1883), 1801.